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Fourier transform infra-red study on the structure of freeze-dried atactic polystyrene from dilute solutions

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The structure of freeze-dried atactic polystyrene (a-PS) prepared from benzene and cyclohexane dilute solutions (0.1 wt%) was investigated by Fourier transform infra-red spectroscopy. The freeze-dried a-PS showed infra-red absorption bands at 1047, 1098 and 1262 cm^{-1}; the last one had been reported for the 3/1 helical structure of isotactic PS in the crystalline state. It was revealed that the above absorption peaks correspond to some specific structure for the freeze-dried a-PS where the chain overlapping is absent in the glassy state. These absorption peaks were also found to be reduced by annealing above T_g, but not changed below T_g. © 1997 Elsevier Science Ltd.

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Introduction

The study on the structures of glassy polymers is one of the interesting topics for the fundamental understanding of the various properties of glassy disordered materials. Atactic polystyrene (a-PS) is a typical glass-forming polymer, and its structure has been extensively studied by various methods, including X-ray scattering[1–4], Fourier transform infra-red (*FT* i.r.) spectroscopy[5–8], Raman scattering[6,8–10], nuclear magnetic resonance (n.m.r.)[11], electron microscopy[12,13], neutron scattering and molecular dynamics simulations[14–16], though its precise structure is not yet fully understood. The X-ray studies on a-PS revealed a scattering peak appearing at $s = 0.75\,\text{Å}^{-1}$ ($s = 4\pi \sin\theta/\lambda$), which is called the polymerization peak and is due to the inter-main-chain (or intermolecular) correlation in the glassy state[1–4]. A unique feature in the X-ray scattering profile of a-PS is that the intermolecular peak is weaker than the main amorphous halo ($1.4\,\text{Å}^{-1}$). With regard to this feature, Mitchell and Windle[4] proposed the so-called superchain model in which strongly interacting phenyl groups are stacked and they cause a specific inter chain interaction. In any case, it should be noted that the structural aspects of the intra- and inter-chain interactions for a-PS are rather different from those of other glassy polymers[17].

In this study, using *FT* i.r. spectroscopy, we investigate the structure of freeze-dried a-PS prepared from rapidly frozen dilute solutions in which the chain overlapping is absent[18]. Xue and co-workers[19,20] revealed that freeze-dried isotactic PS (i-PS) prepared in such a way shows rapid crystallization and high crystallinity. This is due to the absence of the inter-chain interactions which prevent crystallization. Their result suggests that the structure of the freeze-dried a-PS may be different from that of the usual a-PS glass in the contributions of the inter-chain and inter-phenyl group interactions because of the absence of chain overlapping. As will be reported below, we have found an anomalous i.r. absorption spectrum for the freeze-dried a-PS, which may reflect a specific structure due to a unique feature of the chain interactions of the freeze-dried a-PS.

Experimental

We used commercial PS standards of Scientific Polymer Products (a-PS1: $M_n = 12\,400$, $M_w = 13\,700$; a-PS2: $M_n = 109\,900$, $M_w = 114\,200$). The stereoregularity of these samples was determined by the ^{13}C n.m.r. method[21] to be mm : mr : rr = 0.18/0.65/0.17. The sample polymers were dissolved in the solvent (benzene or cyclohexane). These solutions of 0.02–5.0 wt% were rapidly (almost instantaneously) frozen by pouring directly into liquid N_2, and the frozen solvents were then sublimated by a freeze-drying apparatus (Yamato DC-55A). The *FT* i.r. measurements were performed by a Perkin-Elmer Paragon 1000 and a Jasco *FT*/i.r.-8000. Films cast from 5 wt% benzene solutions were also prepared for comparison (for the low molecular weight sample, a power-like sample was obtained instead of a film).

Results and discussion

Figure 1 shows the results of the *FT* i.r. measurements for the cast and freeze-dried a-PS samples prepared from benzene solutions. We can clearly see the appearance of absorption bands at 1047, 1098 and 1262 cm^{-1} for the freeze-dried a-PS. These three i.r. bands are absent in the spectra of the cast samples. The 1262 cm^{-1} i.r. band was found to appear for i-PS in the crystalline state and also in the gel state, but it does not appear in the non-crystalline state of i-PS[5,7]. Thus, the 1262 cm^{-1} peak has been considered to be due to the 3/1 helical structure of the i-PS crystal[5–7]. However, the result shows that this peak appears in the present non-crystalline a-PS, which exhibits no other evidence for the 3/1 helical crystalline structure in the i.r. data (e.g. 922, 587 and 558 cm^{-1}). Therefore, we can conclude that the 1262 cm^{-1} band is not related, at least directly, to the 3/1 helical structure.

In the freeze-dried sample which is prepared from dilute (non-entangled or non-overlapping) solution, the

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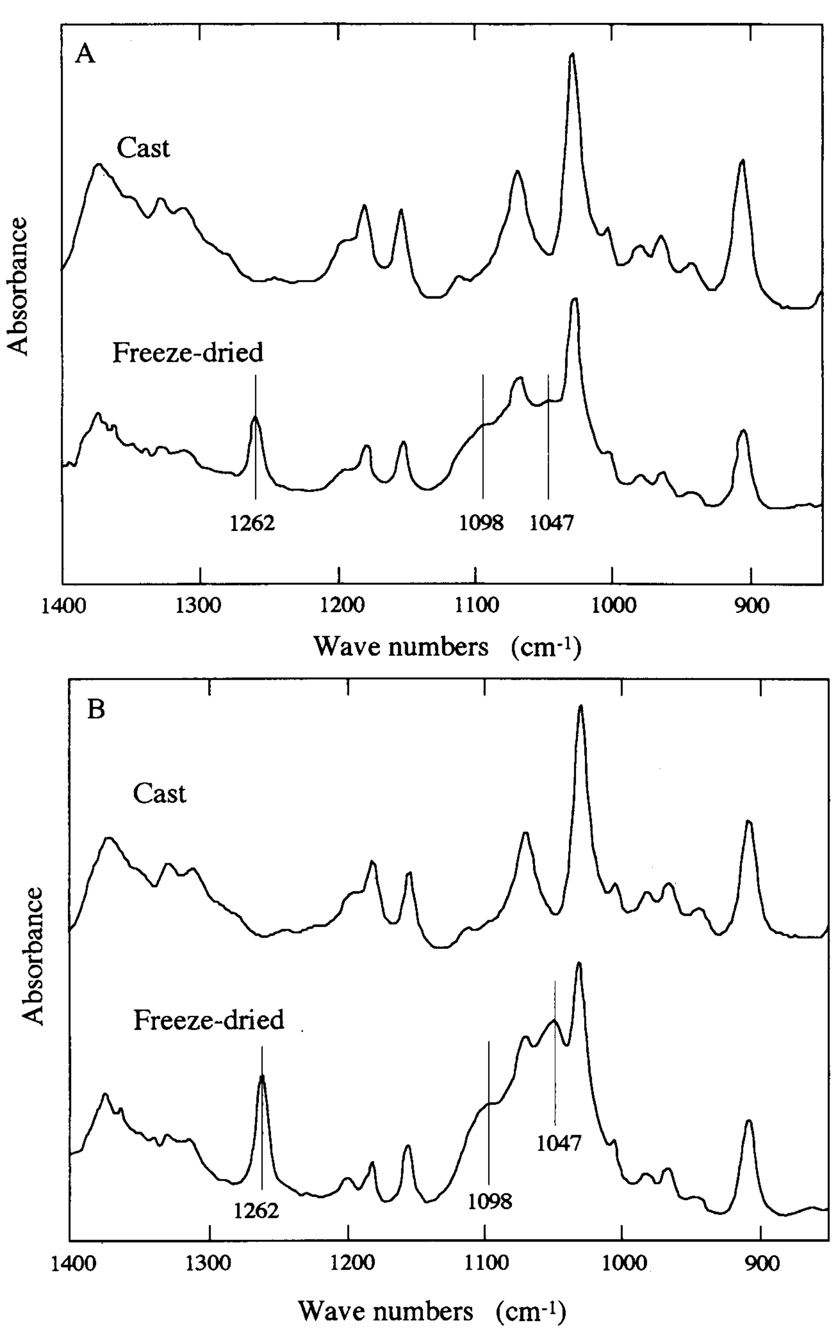

Figure 1 I.r. spectra for a-PS samples (A: $M_n = 12400$; B: $M_n = 109900$). Cast samples were prepared from 5 wt% benzene solutions, and freeze-dried samples were prepared from 0.1 wt% benzene solutions. For freeze-dried samples, absorption peaks appear at 1047, 1098 and 1262 cm^{-1}, which represents a certain specific structure

chain entanglement or the chain overlapping is considered to be still absent in the dried state, and furthermore, the chain dimension is perturbed depending on the solvent used in the freeze-drying process. The present result shows that the structure relevant to 1047, 1098 and 1262 cm^{-1} bands may be easily formed with less overlapping between the chains.

The concentration of the preparation solution affects the i.r. absorption, i.e. we found that the 1047, 1098 and 1262 cm^{-1} bands decrease with increasing concentration and, at above 10 wt%, the three bands do not appear. *Table 1* shows the relative absorbance at 1262 cm^{-1} for the freeze-dried a-PS2 ($M_n = 109900$) prepared from different concentrations of the benzene solution. Here, the relative peak intensity was estimated by taking the 1028 cm^{-1} band (C–H in-plane bending of the phenyl group) as a reference peak. The result suggests that the chain overlapping disturbs the formation of the specific structure relevant to the three bands.

Table 1 Relative i.r. absorbance at 1262 cm^{-1} for freeze-dried a-PS2 prepared from benzene solutions of different concentrations

Concentration (wt%)	Relative absorbance
0.02	3.14
0.1	2.34
1.0	1.09
5.0	0.30

Since the behaviour of the three absorption bands (1047, 1098 and 1262 cm^{-1}) seems to be the same in the

Table 2 Relative i.r. absorbance at 1262 cm^{-1} for freeze-dried a-PS prepared from different solvents (0.1 wt%)

M_n	Freeze-dried from benzene	Freeze-dried from cyclohexane	Cast from benzene
12 400	1.00	0.75	0
109 900	2.34	0.66	0

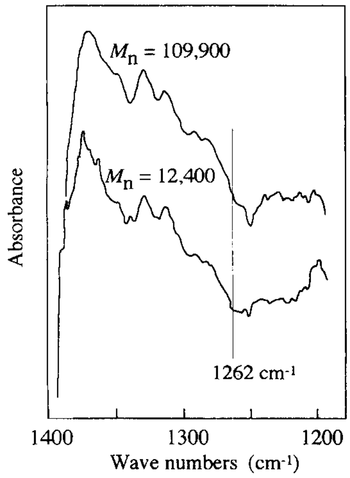

Figure 2 I.r. spectra for a-PS samples in 1 wt% benzene solution. Absorption due to the solvent was subtracted from the data

present study, we treat only the 1262 cm^{-1} band in the quantitative discussion below for the peak intensity. *Table 2* shows the relative absorbance at 1262 cm^{-1} for the samples prepared from 0.1 wt% solutions. For a-PS2 (M_n = 109 900), the concentration of 0.1 wt% seems not to be low enough to avoid completely the chain overlapping, but the freeze-dried a-PS2 from benzene solution shows stronger 1262 cm^{-1} peak intensity than that of a-PS1 (M_n = 12 400). The reason for this result is not clear, but we propose one possible explanation. The specific structure of the freeze-dried a-PS may be formed at a coupling (or interacting) site where two (or more) segments belonging to a same polymer chain come close to each other, and the number of such coupling sites seems to increase with increasing chain length, i.e. the ratio of the intra- to inter-molecular coupling sites is larger for the higher molecular weight. Thus, the specific structure may be formed within a single polymer chain at intra-molecular interacting sites, and is not due to the inter-molecular interaction.

Table 2 also shows a comparison between different preparation solvents (benzene and cyclohexane). It is shown that the 1262 cm^{-1} peak is stronger for the benzene (good solvent) solution than for the cyclohexane (poor solvent) solution. Considering the solvent quality, the chain expansion is larger for the benzene solution than for the cyclohexane solution; thus, we can say that the expanded chain conformation is preferred for forming the specific structure of the freeze-dried a-PS.

It is now important to elucidate how the specific structure of the freeze-dried a-PS is formed. *Figure 2* shows the *FT* i.r. spectra of the present a-PS samples in 1 wt% benzene solution (here, the concentration 1 wt% is larger than that of the previous preparation solution, but we ascertained that the specific i.r. bands still appear even for the freeze-dried a-PS from the 1 wt% solution).

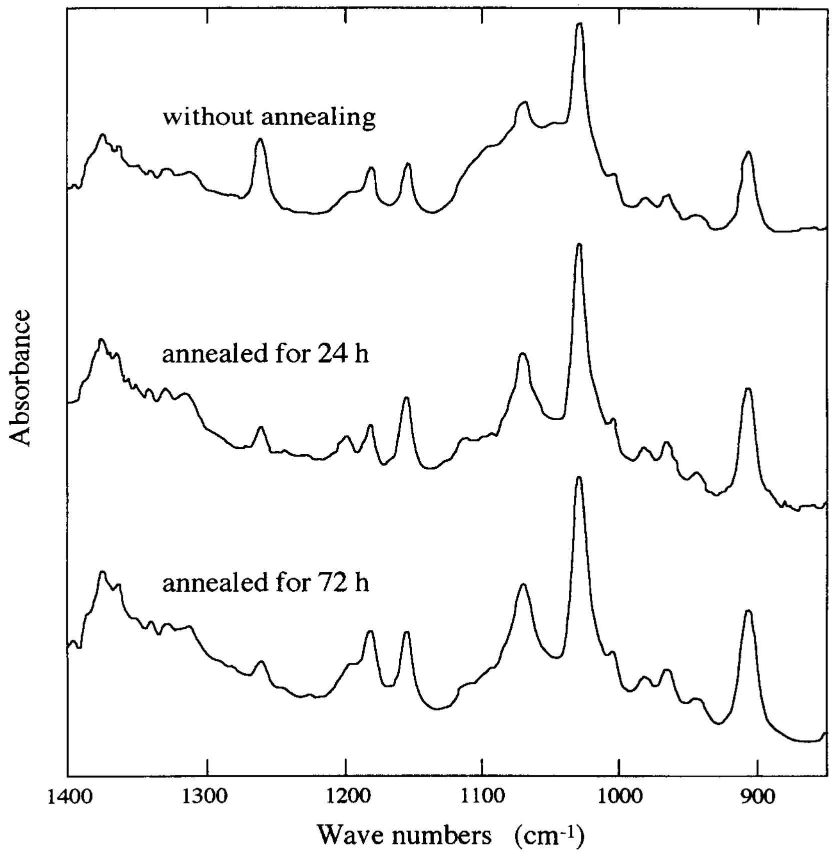

Figure 3 I.r. spectra for freeze-dried a-PS1 (M_n = 12 400) prepared from 0.1 wt% benzene solution with annealing at 130°C

Here, we cannot observe the 1262 cm^{-1} band, which indicates that the precursor for the specific structure of the freeze-dried a-PS does not exist in the benzene solution. We therefore consider that the 1262 cm^{-1} structure is rapidly formed in the freezing process or gradually formed during the solvent sublimation process. The possibility of the chain rearrangements which occur during the quenching and freeze-drying processes for the present a-PS may be very similar to the rapid crystallization of i-PS observed during the same processes (the shock-cooling and freeze-drying)[19,20].

We found that the three peaks decrease when we anneal the freeze-dried a-PS above the glass transition temperature T_g (130°C for 24–72 h) as shown in *Figure 3*, while annealing below T_g (80°C for 72 h) causes no change in the i.r. spectrum. This result suggests that the formation of the structure related to the 1047, 1098 and 1262 cm^{-1} bands of the freeze-dried a-PS requires certain rearrangements of the main chain conformation, i.e. the present specific structure is not the one related only to the side-group arrangements.

In this study, we have shown that the freeze-dried a-PS exhibits three specific absorption bands in the i.r. spectrum. The concrete molecular structure which gives rise to these bands is not clear at the present time, but it has been shown that a certain expanded conformation with no chain overlapping and entanglement is favourable for the formation of the present specific structure. We also found that the specific structure can be easily formed for the higher molecular weight sample. Further investigations on the structure of the freeze-dried a-PS by means of X-ray scattering and *FT*–Raman spectroscopy are currently under investigation, and they will be reported in a forthcoming paper.

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